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PRINCETON UNIV N J DEPT OF CHEMISTRY

NEW SIGMA-ETHYL COMPOUNDS OF DIMOLYBDENUM AND EVIDENCE FOR DINU--ETC(U)

JUN 78 M H CHISHOLM, D A HAITKO, C A MURILLO

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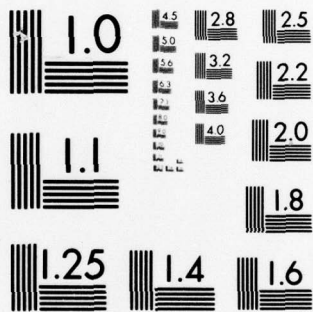
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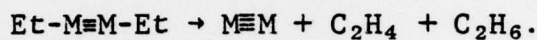
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⁶ New σ -Ethyl Compounds of Dimolybdenum ($M \equiv M$) and
Evidence for Dinuclear Reductive Elimination with a Concomitant
Metal-Metal Triple to Quadruple Bond Transformation:



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C. A./Murillo

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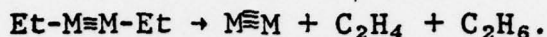
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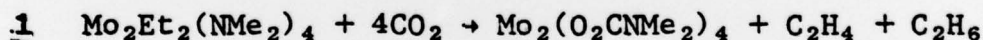
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The preparation and properties of $Mo_2Et_2(NMe_2)_4$ and $Mo_2Et(Obu^t)_5$ are described. Reaction of the former with CO_2 (≥ 4 equiv) leads to $Mo_2(O_2CNMe_2)_4$, C_2H_6 and C_2H_4 .		

New σ -Ethyl Compounds of Dimolybdenum ($M \equiv M$) and
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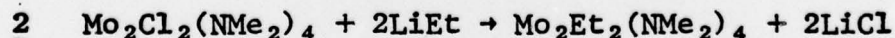


Sir:

Transition metal complexes containing σ -ethyl ligands are prone to thermal decomposition by an initial step involving β -hydrogen elimination:¹ $M-C_2H_5 \rightleftharpoons M-H + C_2H_4$. This reaction is suppressed when the metal is coordinatively saturated and attains an 18-valence shell electronic configuration.² We report here (i) the preparation of the thermally stable σ -ethyl dimolybdenum compounds $Mo_2Et_2(NMe_2)_4$ and $Mo_2Et(Obu^t)_5$, in which the ethyl ligands are coordinated to unsaturated metal centers³ and (ii) the reaction between $Mo_2Et_2(NMe_2)_4$ and CO_2 which proceeds according to eq 1 and provides a model reaction for studies of dinuclear reductive elimination.⁴



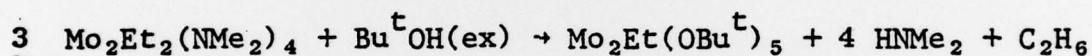
$Mo_2Cl_2(NMe_2)_4$ ⁵ reacts smoothly at $-78^\circ C$ with $EtLi$ (2 equiv) in hydrocarbon solvents to give the yellow, crystalline compound $Mo_2Et_2(NMe_2)_4$ which may be obtained analytically pure⁶ by sublimation ($60-70^\circ C$, 10^{-4} mmHg) in greater than 70% yield based upon eq 2.



The 1H NMR spectrum of $Mo_2Et_2(NMe_2)_4$ obtained in toluene- d_8 at $-61^\circ C$ at 270 MHz is shown in Figure 1. This corresponds to the low temperature limiting spectrum of a mixture of anti and gauche-rotamers of an ethane-like molecule $(Me_2N)_2EtMo \equiv MoEt(NMe_2)_2$.⁷ Note the methylene protons of the gauche rotamer (but not the anti-rotamer)

are diastereotopic and form part of an ABX₃ spectrum. At 90°C rotation about the M-N bonds is rapid on the NMR timescale leading to the coalescence of proximal and distal N-Me signals but rotation about the M≡M bond (anti = gauche isomerization) is still slow. In the mass spectrometer there is a strong molecular ion Mo₂(NMe₂)₄Et₂⁺ (m/e = 430) and an ion Mo₂(NMe₂)₄⁺ (m/e = 372) corresponding to the loss of 2Et.

Mo₂Et₂(NMe₂)₄ reacts rapidly at room temperature with tert-butanol in benzene according to eq 3.



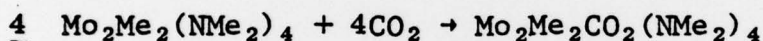
Mo₂Et(OBu^t)₅ is a burgundy-red solid which "sublimes with some decomposition at 60-70°C 10⁻⁴ mmHg. The ¹H NMR spectrum at low temperature (-76°C) at 270 MHz in toluene-d₈ consists of a simple triplet and quartet for the Et ligand and two resonances in the ratio of 3:2 for the OBu^t groups.⁸ This is consistent with an ethane-like molecule (Bu^tO)₂(Et)Mo≡Mo(OBu^t)₃ in which rotation about the Mo≡Mo bond is rapid on the NMR timescale.⁹

Mo₂Et₂(NMe₂)₄ in toluene reacts rapidly with CO₂ (> 4 equiv) to give a pale-yellow finely divided precipitate. This compound has not been structurally characterized but is considered to be Mo₂(O₂CNMe₂)₄ and to have the dimolybdenum tetraacetate structure (M≡M)¹⁰ on the following grounds: (i) analytical data¹¹, (ii) infrared data¹², and (iii) the appearance in the mass spectrum of a very strong ion corresponding to Mo₂(O₂CNMe₂)₄⁺ (this is the ion of highest mass) and the doubly charged ion Mo₂(O₂CNMe₂)₄²⁺. The compound is not appreciably soluble in hydrocarbon solvents, nor CD₂Cl₂, but is sparingly soluble in pyridine.¹³

In a sealed NMR tube reaction Mo₂Et₂(NMe₂)₄ in toluene-d₈ was reacted with CO₂ (> 4 equiv). The finely divided precipitate was centrifuged to the top of the tube and the ¹H NMR spectrum of the clear, virtually colorless solution was recorded.

The only proton signals observed corresponded to ethylene and ethane which were in the integral ratio of 4:6, respectively.¹⁴ We conclude that the reaction between $\text{Mo}_2\text{Et}_2(\text{NMe}_2)_4$ and CO_2 proceeds stoichiometrically according to eq 1 and as such provides a model reaction for detailed studies of dinuclear reductive elimination.¹⁵ A simple intramolecular mechanism involving an initial β -hydride elimination, $\text{Et-Mo}\equiv\text{M-H} + \text{C}_2\text{H}_4$, followed by C-H reductive elimination across the $\text{Mo}\equiv\text{Mo}$ bond, $\text{Et-Mo}\equiv\text{Mo-H} \rightarrow \text{Et-H} + \text{Mo}\equiv\text{Mo}$, satisfies all our observations.

In contrast to the above we find that $\text{Mo}_2\text{Me}_2(\text{NMe}_2)_4$ reacts with CO_2 according to eq 4.



The compound $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4$ ¹⁶ is of sufficient thermal stability to allow the detection of the molecular ion $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4^+$ in the mass spectrometer. In the solid state and in solution $\text{Mo}_2\text{Me}_2(\text{O}_2\text{CNMe}_2)_4$ is believed to share the $\text{W}_2\text{Me}_2(\text{O}_2\text{CNEt}_2)_4$ structure¹⁷ which has a planar C-W-W-C unit with a C-W-W angle equal to 106° .

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 b) P. J. Davidson, M. F. Lappert and R. Pearce, Acc. Chem. Res. 7, 209 (1974).
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2. See, for example, the detailed studies of the thermal reaction
 $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{alkyl}) \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{H})(\text{PPh}_3) + \text{olefin}$:
 D. L. Reger and E. C. Culbertson, J. Am. Chem. Soc. 98, 2789 (1976).
3. In M_2X_6 and $\text{M}_2\text{X}_6\text{-nY}_n$ compounds (X, Y are uninegative monodentate ligands) the metals attain only 12 valence shell electrons as a result of M-X σ bonds and the M-M triple bond. The metals are capable of increasing their coordination number and number of valence electrons by Lewis base association reactions e.g.,
 $\text{Mo}_2(\text{OSiMe}_3)_6 + 2\text{HNMe}_2 \rightleftharpoons \text{Mo}_2(\text{OSiMe}_3)_6(\text{HNMe}_2)_2$ M. H. Chisholm, F. A. Cotton, M. W. Extine and W. W. Reichert, J. Am. Chem. Soc. 100, 153 (1978).
4. For reductive elimination in mononuclear chemistry see C. A. Tolman, Chem. Soc. Rev. 1, 357 (1972).
5. M. Akiyama, M. H. Chisholm, F. A. Cotton, M. W. Extine and C. A. Murillo, Inorg. Chem. 16, 320 (1977). Note all operations must be carried out in dry and oxygen free solvents and atmosphere.
6. Found (Calcd): C, 33.55 (33.79); H, 7.89 (8.04); N, 12.99 (13.15).
7. See the structural and dynamic behavior of the related compound $\text{W}_2\text{Me}_2(\text{NEt}_2)_4$: M. H. Chisholm, F. A. Cotton, M. W. Extine, M. Millar and B. R. Stults, Inorg. Chem. 15, 2244 (1976).
8. Et group: $\delta(\text{CH}_2) = 2.98$, $\delta(\text{CH}_3) = 1.78$, $J_{(\text{HH})} = 7.9\text{Hz}$.
 OBu^t groups at -76°C : $\delta = 1.60$ and 1.56 in the integral ratio 3:2, respectively. Chemical shifts (δ) given in ppm downfield from TMS.
9. Accidental magnetic degeneracy could account for the observed 3:2 spectrum (c.f. predicted low temperature limiting spectrum 2:2:1).

10. For a recent review of compounds containing M-M quadruple bonds see F. A. Cotton, Chem. Soc. Rev. 4, 27 (1975) (b) The diethylcarbamate $\text{Cr}_2(\text{O}_2\text{CNEt}_2)_4 \cdot (\text{HNEt}_2)_2$ has recently been structurally characterized and shown to have a $\text{Cr}\equiv\text{Cr}$ bond. M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, Inorg. Chem., submitted for publication.
11. Found (Calcd): C, 26.23 (26.48); H, 4.25 (4.44); N, 10.09 (10.29).
12. In particular the presence of a strong absorption at 1560 cm^{-1} assignable to $\nu(\text{NCO}_2)$ of a bridging bidentate carbamate ligand. See M. H. Chisholm and M. W. Extine, J. Am. Chem. Soc. 99, 782 (1977).
13. ^1H nmr data recorded at 100MHz, 25°C in pyridine- d_5 : $\delta(\text{O}_2\text{CNMe}_2) = 2.93$ ppm relative to TMS.
14. Found by weighing the traces 38:62. Any departure from the predicted ratio, 4:6, may be due to their differing solubilities.
15. Labelling studies are planned in order to investigate (i) the reversibility of β -hydrogen elimination and (ii) the intra vs. intermolecular nature of the reaction.
16. Analysis Found (Calcd): C, 29.50 (29.29); H, 5.14 (5.23); M, 9.65 (9.75).
17. M. H. Chisholm, F. A. Cotton, M. W. Extine and B. R. Stults, Inorg. Chem. 16, 603 (1977).
18. Alfred P. Sloan Fellow, 1976-78.

Caption to Figure 1

^1H nmr spectrum of a mixture of anti- and gauche-
 $\text{Et}(\text{Me}_2\text{N})_2\text{Mo}\equiv\text{Mo}(\text{NMe}_2)_2\text{Et}$ recorded in toluene- d_8 at -61°C
and 270MHz.

¹H

(*)anti & gauche - Mo₂(σ-C₂H₅)₂(NMe₂)₄

